Distribution and Accumulation of Chromium in the Sediments of the Kaohsiung Ocean Disposal Site, Taiwan

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Abstract

The distribution, enrichment, and accumulation of chromium (Cr) in the sediments of Kaohsiung Ocean Disposal Site (KODS), Taiwan were investigated. Sediment samples from two outer disposal site stations and nine disposed stations in the KODS were collected per quarterly in 2009 and characterized for Cr, aluminum (Al), organic matter, and grain size. Results showed that the mean Cr concentrations varied from 20.0 to 60.0 mg/kg. Cr concentrations at the disposed stations were slightly higher than those at outer disposal site. The accumulation factor and potential ecological risk index indicate that the sediments at disposed area centers have the minor degree of Cr accumulation and the low ecological potential risk. All observed data showed that the disposed area centers may be subjected to the disposal impaction of harbor dredged sediments as we can tell.

Keywords

Ocean Dispose; Chromium; Enrichment Factor; Potential Ecological Risk Index

Introduction

Kaohsiung Harbor is located on the southwestern shore, and it is the largest international harbor in Taiwan. There are four major rivers, namely Love River, Canon River, Jen-Gen River, and Salt River flow into the harbor that bring in a large quantity of suspended solids and other pollutants. As a result, a fast accumulation of sediment particles in the harbor occurs and periodical dredging of harbor sediments is necessary in order to maintain navigation in the harbor. Millions cubic meters of sediments are dredged annually. Currently, all dredged sediments from the Kaohsiung Harbor are dumped into the ocean at a specific area, Kaohsiung Ocean Disposal Site (KODS), designated by Taiwan Environmental Protection Agency (TEPA). Approximately 30 million cubic meter sediment were dredged and transported to the disposal area annually. The KODS was established since 2003. It is totally about 210 million cubic meter disposal already since the starting.

Kaohsiung Harbor is located adjacent to Kaohsiung City, which is the largest industrial city in southern Taiwan with a population of over 1.5 million. Currently, the city sewage system serves about 42% of the metropolis (Chen et al., 2012). Thus, about 58% domestic wastewater is discharged directly into receiving water bodies without adequate treatment. Moreover, several industrial plants (e.g. metal processing factories, paint and dye industries, chemical manufacturing plants, electronic industries, motor vehicle plating and finishing plants, paper and board mills, and foundries) located in or adjacent to Kaohsiung City (Chen et al., 2007; Chen et al., 2012) discharge industrial wastewater effluents into the receiving bodies. It makes the port showing the phenomenon of heavy metals accumulation in sediments. Previous studies pointed out that the port of sediment accumulated high concentrations of chromium (Cr) contents of 45.8–542.6 mg/kg, showed that the extent of Cr contamination was at the level of intermediate to strong (Chen et al., 2012).

However, when dumping harbor sediments into ocean, it simultaneously leads Cr releasing into the nearby water environment and ocean system, in which Cr is considered serious pollutant by its toxicity, cumulative and non-biodegradable characteristics in water environment. Thus, quality assessments of sediments in ocean dumping area are needed for further understanding of Cr accumulation in sediments ecological system and its impaction upon the environment.

Materials and Methods

Study Area and Sampling

The study area, KODS off of southwestern Taiwan occupies 36 km^2 east of Kaohsiung Harbor at water depths of 500–700 m (Fig. 1), was established since 2003. It is totally about 210 million cubic meter disposal already since the starting. Eleven sampling stations selected in this study included two outer disposal site stations (S10 and S11 were reference stations) and nine disposed stations (S1, S2, S3, S4 were disposal site vertex angle, S5 was disposal site center and S6, S7, S8, S9 were disposed area centers, Fig. 1). The Ocean Researcher III was hired to collect the sediment samples from various locations in the KODS during March, May, August, and October in 2009. About 3 kg of sediments were collected with an SIHPEK grab sampler. Immediately after collection, the samples were transferred into polyethylene bags and kept in an ice box and then transported to the laboratory for analysis. In the laboratory, the samples were kept at to -20º C until further processing and analysis.

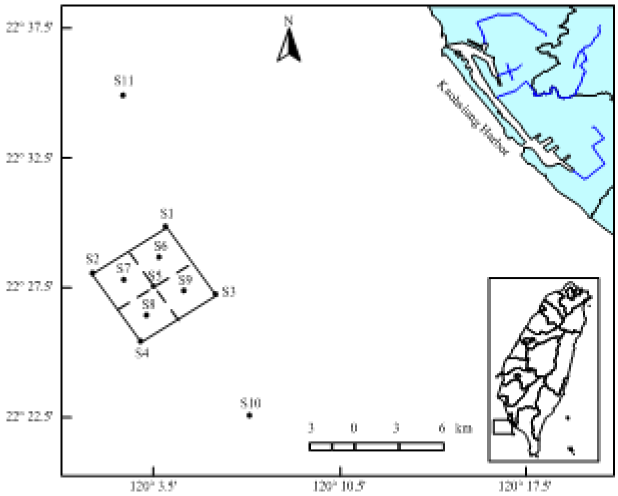

FIG. 1 STUDY AREA AND SAMPLING SITES.

Sample Processing and Analysis

Sediment samples were first screened through a 1-mm nylon net to remove particles with diameters larger than 1 mm. One portion of the screened portion was subject to particle size analyses using a Coulter LS Particle Size Analyzer; the particles were classified into three groups, i.e. clay (<2 μm), silt (2 – 63 μm), and sand (>63 μm). Another portion was washed with ultra-pure water to remove sea salt; the salt-free particles were dried naturally in a dark place, grounded into fine powder with mortar and pestle made of agate (Retsch RM 100 Motor Grinder), and then analyzed for organic matter (OM), Cr, and aluminum (Al). OM was determined using the LOI (loss-on-ignition) method at 550º C; For Al and Cr analyses, 1.0 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids (HNO_3: HCl = 1:3), and was then heated to digest. The digested sample was filter through 0.45 μm filter paper; the filtrate was diluted with ultra-pure water to a pre-selected final volume. The Al and Cr contents were determined using a flame atomic absorption spectrophotometry (Hitachi Z-6100). Each batch of analyses was accompanied with a standard reference (marine sediment (PACS-2)) and a blank. For every 5 samples analyzed, the examination of standard solutions was carried out to assure the stability of the instrument used. The standard reference of marine sediment (PACS-2) was found to contain 91.7±1.9 mg/kg in our lab that is close to the certified values of 90.7±4.6 mg/kg (n = 3).

Data Analyses

Statistical data analyses include average, standard deviation, maximum and minimum. The linear correlation of Pearson technique was used to analyze the correlation between sediment characteristics and Cr concentration implemented with the SPSS 12.0 software. In this study, the enrichment factor (EF) and geo-accumulation index (I_{geo}) were applied to evaluate the degree of Cr pollution and the associated potential ecological risk index (PERI). EF is defined as:

$$EF = (X/Al)_{sediment}/(X/Al)_{crust} \tag{1}$$

Where (X/Al) is the ratio of Hg to Al. The average Al content in the earth crust was excerpted from the data published by Taylor (1964).

The I_{geo} is defined as (Müller, 1981):

$$I_{geo} = log_2\ (C_n / 1.5B_n) \tag{2}$$

Where C_n is the measured content of Cr, and B_n is the background content of Cr in the average shale. Factor 1.5 is the background matrix correction factor due to lithogenic effects.

The potential ecological risk index PERI is defined as (Hakanson, 1980):

$$PERI = PI \times T_i \tag{3}$$

$$PI = C_i / C_f \tag{4}$$

Where PI is the pollution index of Cr; T_i is its corresponding coefficient, i.e. 2 for Cr (Zhao et al., 2005); C_i is the measure concentration of Cr in sediment; C_f is the background concentration of Cr. In this study, the average Cr concentration in the bottom core sediment (80 cm) of 15 mg/kg (Yang, 2009) was taken as the Cr background concentration.

TABLE I MEAN SEDIMENT CHARACTERISTICS AND CHROMIUM CONTENTS IN THE SEDIMENTS OF THE KAOHSIUNG OCEAN DISPOSAL SITE

Area[a]	Site	Longitude (East)	Latitude (North)	Clay (%)		Silt (%)		Sand (%)		OM (%)		Al (%)		Cr (mg/kg)	
				mean	SD[b]	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
I	S1	120° 04.30'	22° 30.06'	17.8	1.0	81.6	2.1	0.6	1.1	2.3	0.9	3.44	0.24	21.6	13.3
	S2	120° 01.42'	22° 28.18'	19.3	1.7	78.5	3.0	2.0	1.4	3.2	1.7	3.30	0.39	24.3	11.9
	S3	120° 06.36'	22° 27.31'	17.7	1.1	80.7	0.7	1.6	1.6	3.4	2.0	3.37	0.26	27.6	2.8
	S4	120° 03.36'	22° 25.42'	17.5	0.6	81.6	0.9	0.9	0.9	4.1	1.7	3.17	0.42	25.8	1.2
II	S5	120° 03.59'	22° 27.57'	15.6	6.7	66.2	28.3	18.2	34.8	2.1	0.9	3.19	0.13	28.3	17.1
III	S6	120° 03.95'	22° 28.82'	17.4	0.7	80.8	2.6	1.8	2.1	4.1	1.2	3.76	0.13	37.4	21.1
	S7	120° 02.51'	22° 27.88'	18.4	1.3	80.8	0.9	0.8	0.4	3.3	1.7	3.10	0.40	54.4	22.7
	S8	120° 03.48'	22° 26.50'	17.5	0.7	81.9	1.7	0.6	1.1	3.4	1.4	3.34	0.23	34.9	7.1
	S9	120° 04.98'	22° 27.44'	18.2	1.1	81.6	1.5	0.2	0.4	3.8	1.1	3.34	0.54	60.0	65.2
R1	S10	120° 07.48'	22° 23.00'	19.0	1.7	79.8	1.4	1.2	0.7	3.4	1.5	3.36	0.33	21.5	0.5
R2	S11	120° 02.45'	22° 34.77'	17.4	1.1	79.0	4.6	3.7	4.7	2.8	1.5	3.24	0.23	14.7	3.0

a. I: disposal site vertex angle, II: disposal site center, III: disposed area centers, and R: outer disposal site.

b. standard deviations

Results and Discussion

Sediment Characteristics and Metal Concentrations

Table I showed the grain sizes of sediment samples in the KODS at 2009. The major particles in all sediment samples are silt with diameter between 2 μm to 63 μm. The percentage compositions are 67.0–81.7% for silt, 13.8–18.9% for Clay (<2 μm), and 0.2–18.2% for sand. The grain sizes distribution showed that the sediments in the KODS were composed by fine grained dominated. However, the standard deviations of grain sizes for every single disposed station varied slightly from time to time. This could be seen especially in station S5. On the other hand, the observation values of OM contents in all sediment samples from the KODS at 2009 ranged from 2.1 to 4.1%.

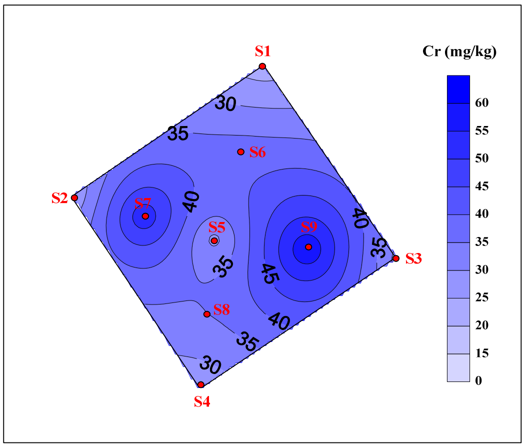

FIG. 2 CONTOUR MAP OF SURFACE SEDIMENT CR CONTENTS IN KAOHSIUNG OCEAN DISPOSAL SITE.

All sediment samples collected from the KODS mean contain 20.0–60.0mg/kg of Cr. The highest concentration of Cr was of disposal area: stations 6, 7, 8, and 9 (Table I). The variances of Cr in disposed area centers (Area III) were higher than those of the disposal site vertex angle (Area I), disposal site center (Area II), and outer disposal site (Area R) while the variances of stations were among the lowest. Concentration distributions of Cr in KODS sediment shown in Figure 2 reveal that the sediment Cr content is relatively higher near the disposed area centers. The sediment Cr content is not obviously correlated to sediment characteristics (Table II). All observed data showed that all stations in the KODS at 2009 may be subjected to the disposal impaction of harbor dredged sediments as we can tell.

TABLE II PEARSON CORRELATION COEFFICIENTS AMONG SEDIMENT CHARACTERISTICS AND CHROMIUM CONCENTRATIONS (N = 44)

	Clay	Silt	Sand	OM	Al
Silt	0.735[a]				
Sand	-0.827[a]	-0.989[a]			
OM	0.035	0.066	-0.065		
Al	0.193	0.017	-0.057	0.467[a]	
Cr	0.067	0.157	-0.145	0.073	0.090

a. Correlation is significant at the 0.01 level (2-tailed).

b. Correlation is significant at the 0.05 level (2-tailed).

Comparison with Sediment Quality Guidelines

Several numerical sediment quality guidelines have been developed for assessing the contamination levels and the biological significance of chemical pollutants recently (Long et al., 1995; Riba et al., 2004). One of the widely used sediment toxicity screening guideline of the US National Oceanic and Atmospheric Administration provides two target values to estimate potential biological effects: effects range low (ERL) and effect range median (ERM) (Long et al., 1995). The guideline was developed by comparing various sediment toxicity responses of marine organisms or communities with observed metals concentrations in sediments. These two values delineate three concentration ranges for each

particular chemical. When the concentration is below the ERL, it indicates that the biological effect is rare. If concentration equals to or greater than the ERL but below the ERM, it indicates that a biological effect would occur occasionally. Concentrations at or above the ERM indicate that a negative biological effect would frequently occur. Fig. 3 shows the measured concentrations of Cr in comparison with the ERM and ERL values. Among the 44 sediment samples collected, the Cr is between ERL (81mg/kg) and ERM (370mg/kg) in 2 samples (4.5%). This indicates that the concentration of Cr found in the sediments may cause adverse impact on aquatic lives. All other sediments are blower ERL, indicates that the biological effect is rare.

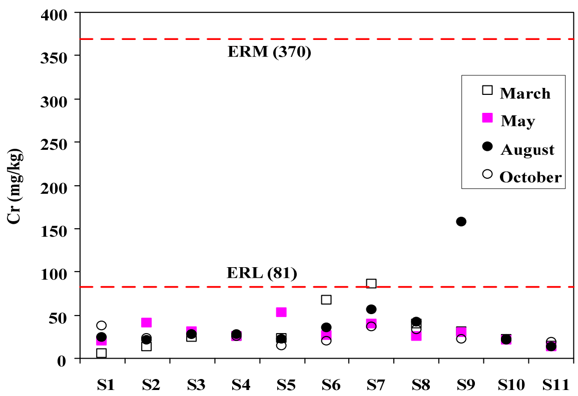

FIG. 3 DISTRIBUTION OF CR CONTENTS IN SURFACE SEDIMENT OF KAOHSIUNG OCEAN DISPOSAL SITE.

Enrichment Factor

The enrichment factor (EF) is a useful tool for differentiating the man-made and natural sources of metal contamination (Morillo et al., 2004; Adamo et al., 2005; Valdés et al., 2005). This evaluating technique is carried out by normalizing the metal concentration based on geological characteristics of sediment. Aluminum is a major metallic element found in the earth crust; its concentration is somewhat high in sediments and is not affected by man-made factors. Thus, Al has been widely used for normalizing the metal concentration in sediments (Chen et al., 2007; Huang & Lin, 2003). When the EF of a metal is greater than 1, the metal in the sediment originates from man-made activities, and vice versa. The EF value can be classified into 7 categories (Birth, 2003): no enrichment for EF <1, minor for EF <3, moderate for EF = 3–5, moderately severe for EF = 5–10, severe for EF = 10–25, very severe for EF = 25–50, and extremely severe for EF >50. Table II show EF values of the sediment Cr for the KODS; the Cr concentration is consistent with the Cr EF value for all sampling stations. In the Stations 7 and 9, EF values are greater than 1, indicates that the sediment Cr has enrichment phenomenon with respect to the earth crust and that Cr originates from man-made sources. Except Stations 7 and 9 that has minor enrichment of Cr, all other sampling stations are classified as no enrichment. Based on the I_{geo} data and Muller's geo-accumulation indexes, the contamination level with respect to Cr at each station is ranked in Table II. Based on the above observations, sediments at the disposed stations (Stations 1–9) was minor polluted. These results point out that the sediment near disposed site experiences minor accumulation of Cr that originates from the dredged sediment of Kaohsiung Harbor.

Assessment of Potential Ecological Risk

TABLE III EF AND I_{GEO} CLASSES OF CHROMIUM FOR EACH STATION STUDIED AT THE KAOHSIUNG OCEAN DISPOSAL SITE

Area[a]	Site	EF	EF class[b]	I_{geo}	I_{geo} class[c]
I	S1	0.5	0	-0.36	0
	S2	0.6	0	-0.01	0
	S3	0.7	0	0.29	1
	S4	0.7	0	0.20	1
II	S5	0.7	0	0.16	1
III	S6	0.8	0	0.58	1
	S7	1.5	1	1.19	2
	S8	0.9	0	0.61	1
	S9	1.4	1	0.91	1
R1	S10	0.5	0	-0.17	0
R2	S11	0.4	0	-0.64	0

a. I: disposal site vertex angle, II: disposal site center, III: disposed area centers, and R: outer disposal site.

b. 0: EF <1 (no enrichment), 1: EF <3 (minor), 2: EF = 3–5 (moderate), 3: EF = 5–10 (moderately severe), 4: EF = 10–25 (severe), 5: EF = 25–50 (very severe), and 6: EF >50 (extremely severe) (Birth, 2003).

c. 0: I_{geo} <0 (none), 1: I_{geo} = 0–1 (none to medium), 2: I_{geo} = 1–2 (moderate), 3: I_{geo} = 2–3 (moderately to strong), 4: I_{geo} = 3–4 (strongly polluted), 5: I_{geo} = 4–5 (strong to very strong), and 6: I_{geo} >5 (very strong) (Müller, 1981).

TABLE IV POLLUTION INDEX AND POTENTIAL ECOLOGICAL RISK INDEX FOR CHROMIUM IN SEDIMENTS FROM THE KAOHSIUNG OCEAN DISPOSAL SITE

Area[a]	Site	PI	PERI	Risk level[b]
I	S1	1.4	2.9	low risk
	S2	1.6	3.2	low risk
	S3	1.8	3.7	low risk
	S4	1.7	3.4	low risk
II	S5	1.9	3.8	low risk
III	S6	2.5	5.0	low risk
	S7	3.6	7.3	low risk
	S8	2.3	4.7	low risk
	S9	4.0	8.0	low risk
R1	S10	1.4	2.9	low risk
R2	S11	1.0	2.0	low risk

a. I: disposal site vertex angle, II: disposal site center, III: disposed area centers, and R: outer disposal site.

b. PERI < 40 indicates low risk, 40 ≤ PERI < 80 is moderate risk, 80 ≤ PERI < 160 is higher risk, 160 ≤ PERI < 320 is high risk, and PERI ≥ 320 is serious risk (Hakanson, 1980).

The potential ecological risk index (PERI) is applied to evaluate the potential risk associated with the accumulation of Cr in sediments. PERI that was proposed by Hakanson (1980) can be used to evaluate the potential risk of one metal or combination of multiple metals. The calculated PERI values can be categorized into 5 classes of potential ecological risks: low risk (PERI < 40), moderate risk (40 ≤ PERI < 80), higher risk (80 ≤ PERI < 160), high risk (160 ≤ PERI < 320), and serious risk (PERI ≥ 320). Table III lists the PI value, PERI value, and risk classification of the Cr contained in the sediment samples collected in the KODS. All the areas are classified as low risk with respect to Cr pollution. The above evaluation results indicate that the Cr contained in sediments at the KODS has low potential ecological risks. However, the mean PERI value in disposed area centers (Area III) is higher than other sites (Table III).

Conlusions

The sediment samples collected at all sampling stations at the KODS contain 20.0–60.0 mg/kg of Cr. The highest concentration of Cr was of disposed area centers. Results of EF and I_{geo} analyses indicate that the KODS sediments were minor contaminated with Cr. Results of potential ecological risk evaluation show that the classification of potential ecological risk for the sediment Cr at the KODS is low risk. The results can provide regulatory valuable information to be referenced for developing future strategies to renovate and manage ocean disposal site.

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